LA-UR-21-27289

Approved for public release; distribution is unlimited.

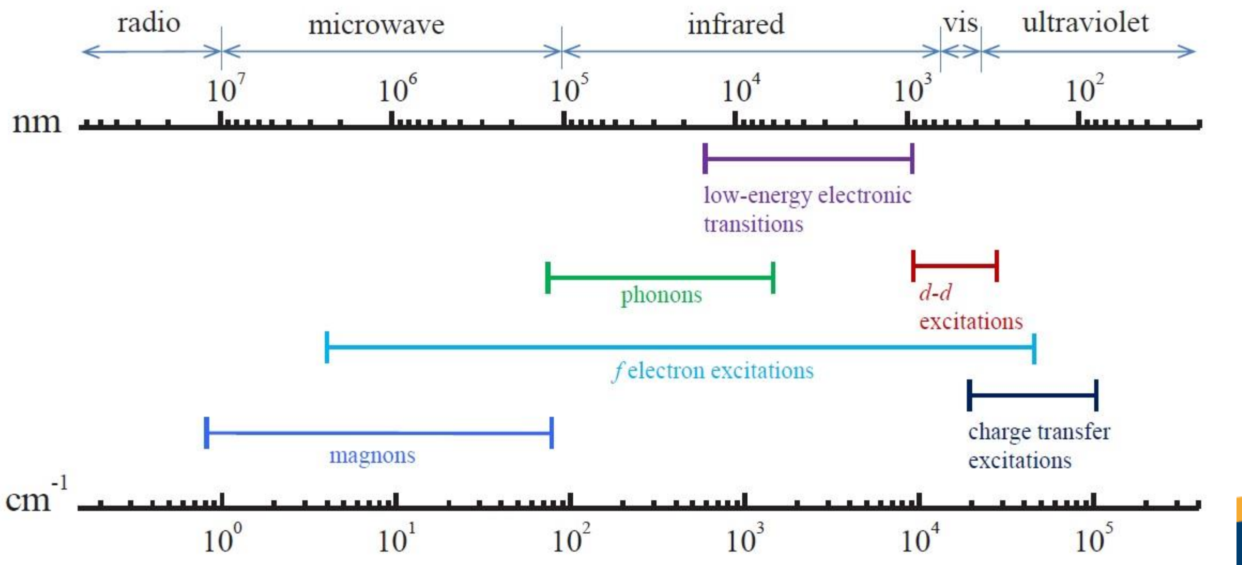
Title:	Understanding materials in extreme conditions via spectroscopy
Author(s):	O'Neal, Kenneth Robert
Intended for:	Job interview technical presentation
Issued:	2021-07-26

Understanding materials in extreme conditions via spectroscopy

Ken O'Neal

Spectroscopy

- Study of light-matter interaction
  - Light can be absorbed, transmitted, reflected, refracted, emitted, etc.
- Probes a wide variety of properties depending on wavelength of light
- Can be static or dynamic



Outline

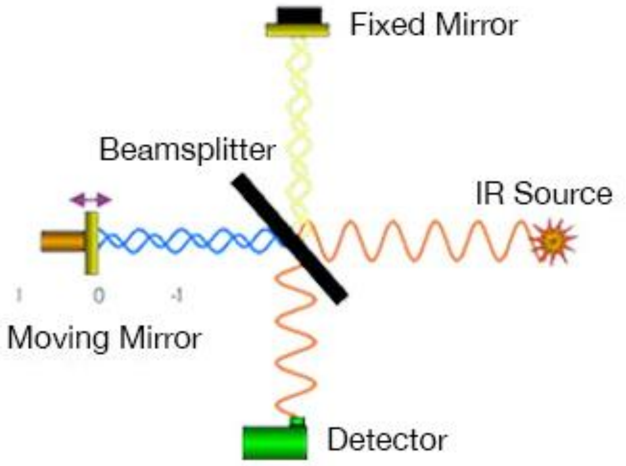
- **FTIR and Raman**
  - Pressure-induced dimensionality crossover in Cu-3Cl(pyd)
  - Local structure changes in Ni_3TeO_6 under pressure
  - Size-dependent vibronic coupling in $CuGeO_3$ nanorods

- Ultrafast spectroscopy
  - Carrier dynamics of $EuCd_2As_2$

- Summary and Acknowledgements

Fourier Transform Infrared Spectroscopy

- Source beam is split into two
  - One goes to fixed mirror; other to moving mirror
  - Switches between destructive and constructive interference
- Recombined beam is passed to sample
  - Can do transmittance (absorbance) or reflectance
- Resulting interferogram is Fourier transformed to get a spectrum in the frequency domain
- Can be used to measure over broad spectral ranges



FTIR instruments

- Different configurations for different types of measurements
  - Varying spectral ranges and resolution, spatial resolution, etc.
- Can measure different sample forms (liquid, crystalline, powders)
- Can couple in cryostats for temperature control

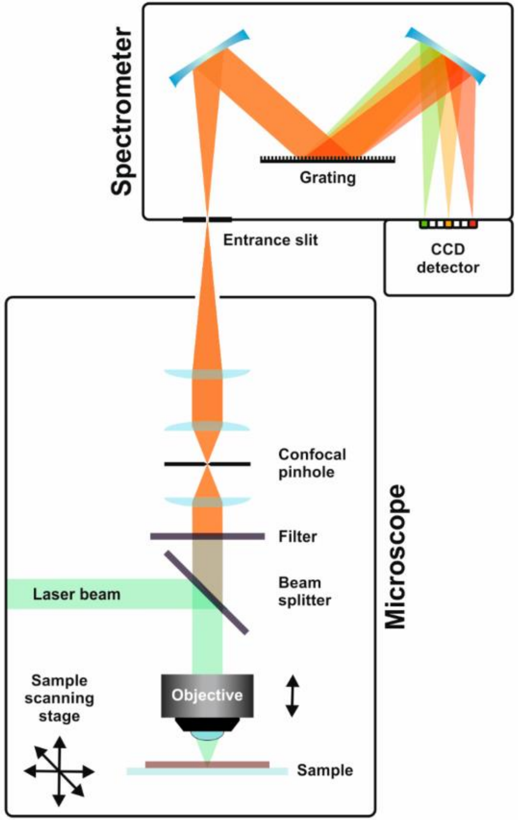
Raman scattering

- Similar spectral ranges but different principle than FTIR

- Excite with one laser wavelength
  - Choice can affect spectra if it is near a resonance

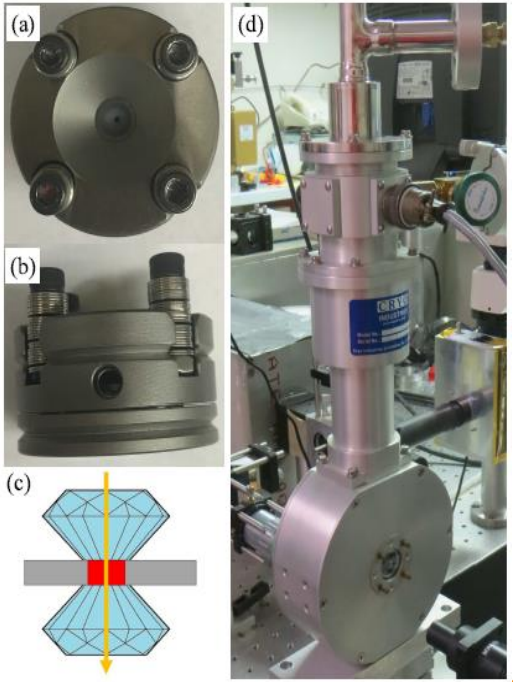
- Measure in relative frequency (with laser line being 0 cm^{-1})
  - Difficult to get to very low frequencies

- Can integrate over time to overcome low signal issues
  - Makes intensity relative



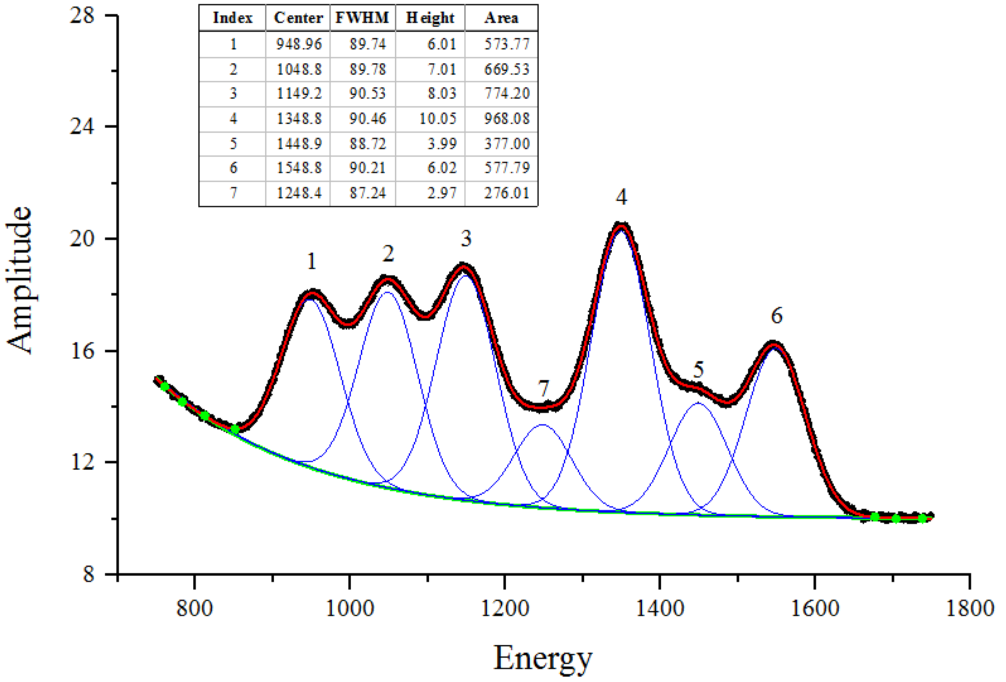
Measuring in extreme conditions

- Temperature (4.2 to 300 K)
  - Open-flow helium cryostat
- Magnetic field (done at NHMFL)
  - 35 T static fields
  - Up to 60 T pulsed fields
- Pressure (ambient to 20 GPa)
  - Diamond anvil cell
- Combine parameters to map out phase space



Analyzing spectra

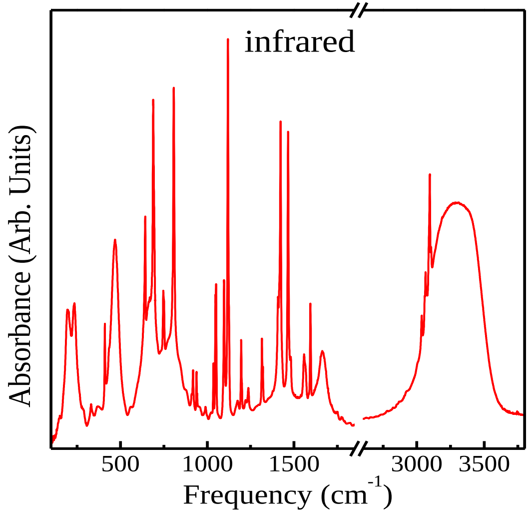
- Fit spectra with standard functions
- Extract peak information depending on scientific interest
  - Center, fullwidth at half max, area
- Tracking as function of tuning parameter can reveal transitions
- Can be used to quantify coupling constants, fit to models, etc.

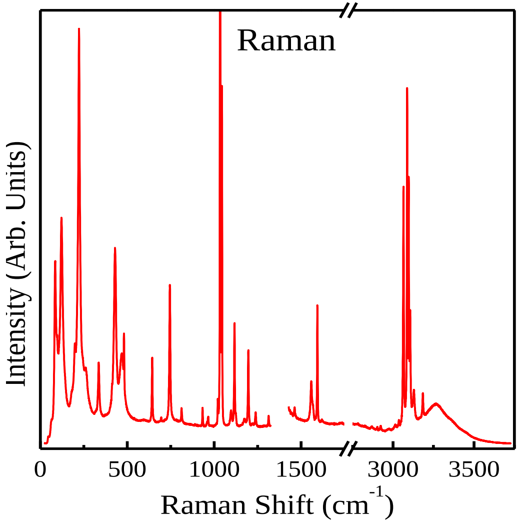


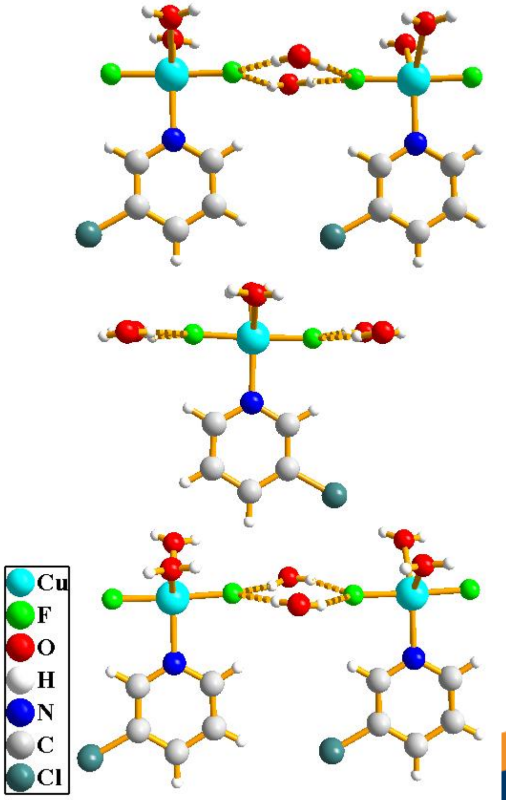
Index	Center	FWHM	Height	Area
1	948.96	89.74	6.01	573.77
2	1048.8	89.78	7.01	669.53
3	1149.2	90.53	8.03	774.20
4	1348.8	90.46	10.05	968.08
5	1448.9	88.72	3.99	377.00
6	1548.8	90.21	6.02	577.79
7	1248.4	87.24	2.97	276.01

$CuF_2(H_2O)_2$(3-chloropyridine)

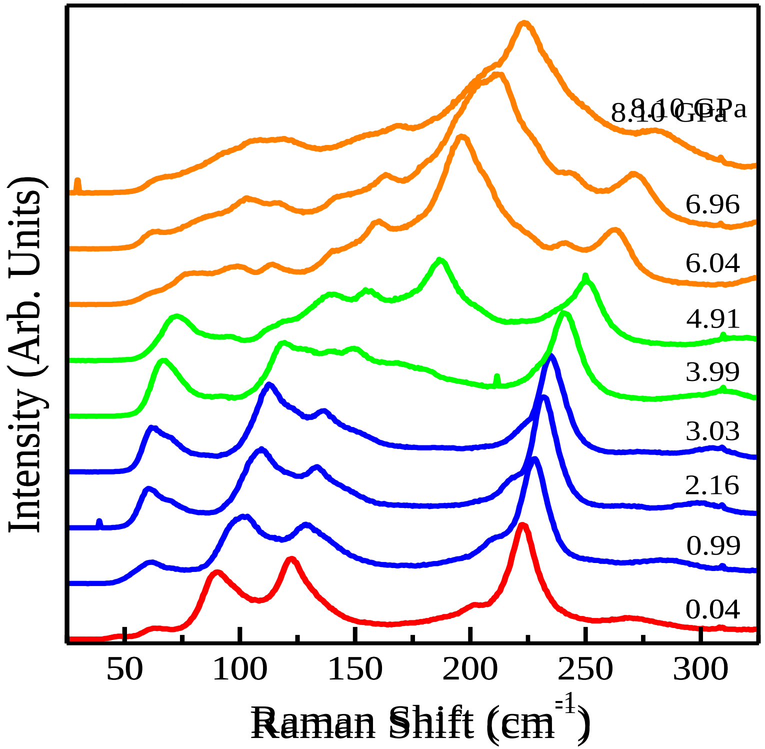
- Two-dimensional molecule-based magnet
  - Magnetic exchange within Cu-F-H_2O plane
- Magnetic crossover from AFM to FM at 0.8 GPa
- Complex spectra – many peaks in both IR and Raman

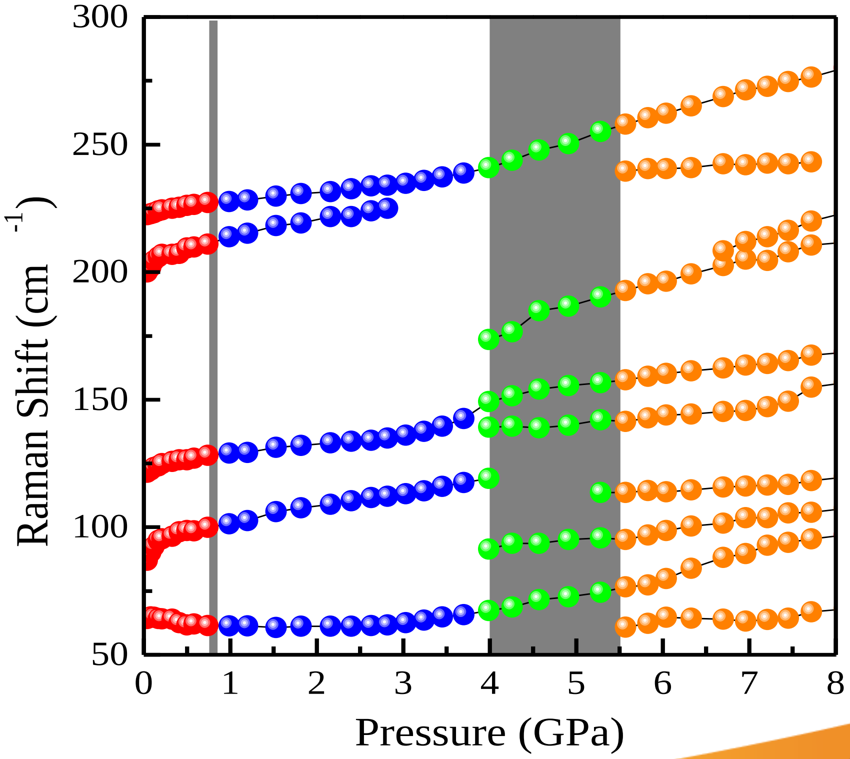






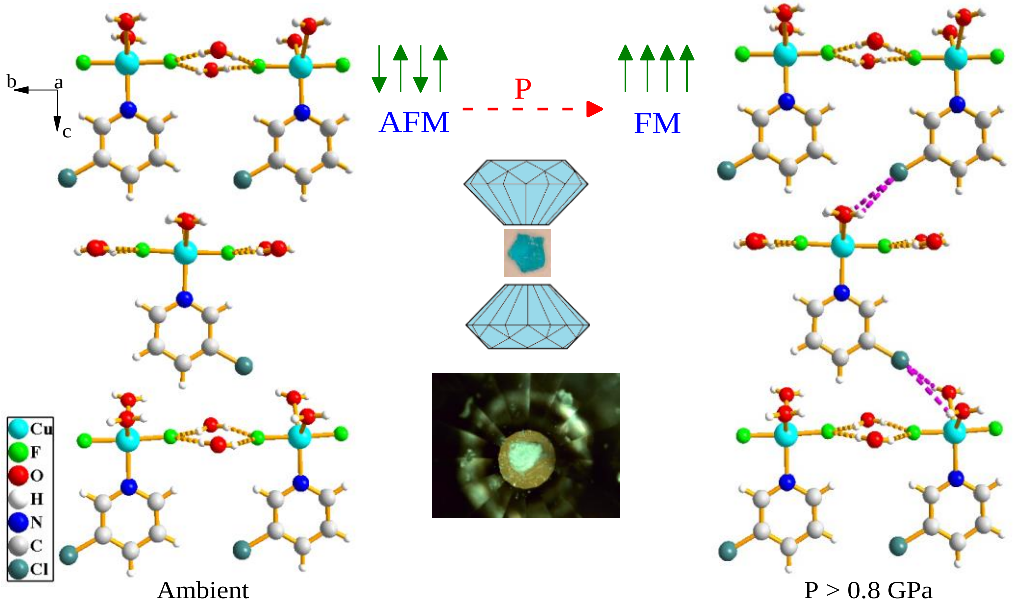
What do the high pressure spectra show?





What do we learn?

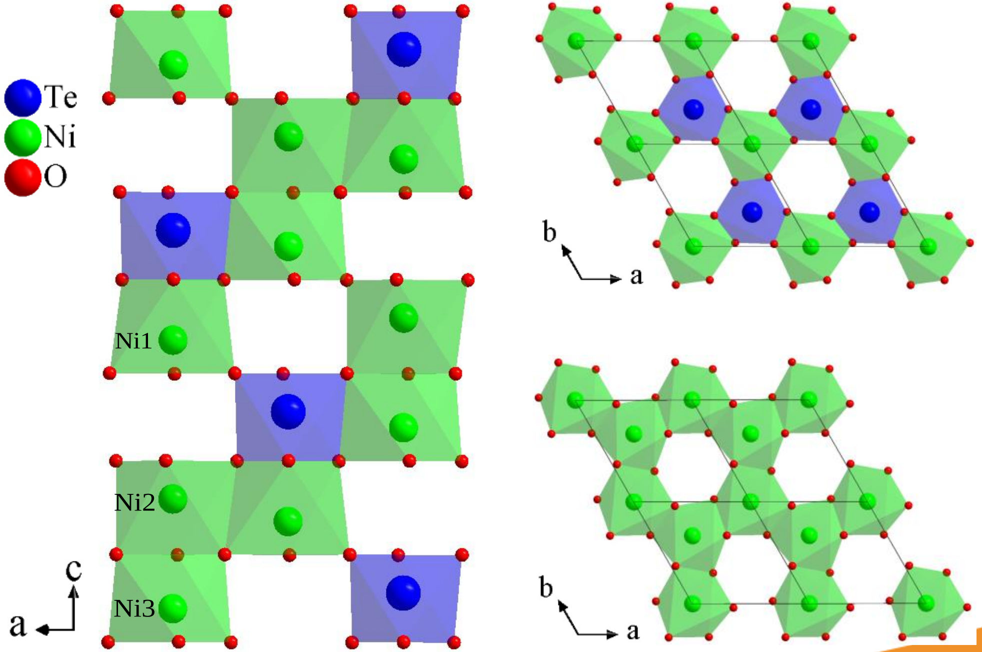
- Combined IR, Raman, and calculations to get full picture
- New hydrogen bond formed under pressure with Cl
- New magnetic exchange pathway
  - Material goes from 2D to 3D
  - Magnetism changes from AFM to FM
- New structural transition discovered near 5.5 GPa



O'Neal, Sci. Rep. **4**, 6054 (2014)

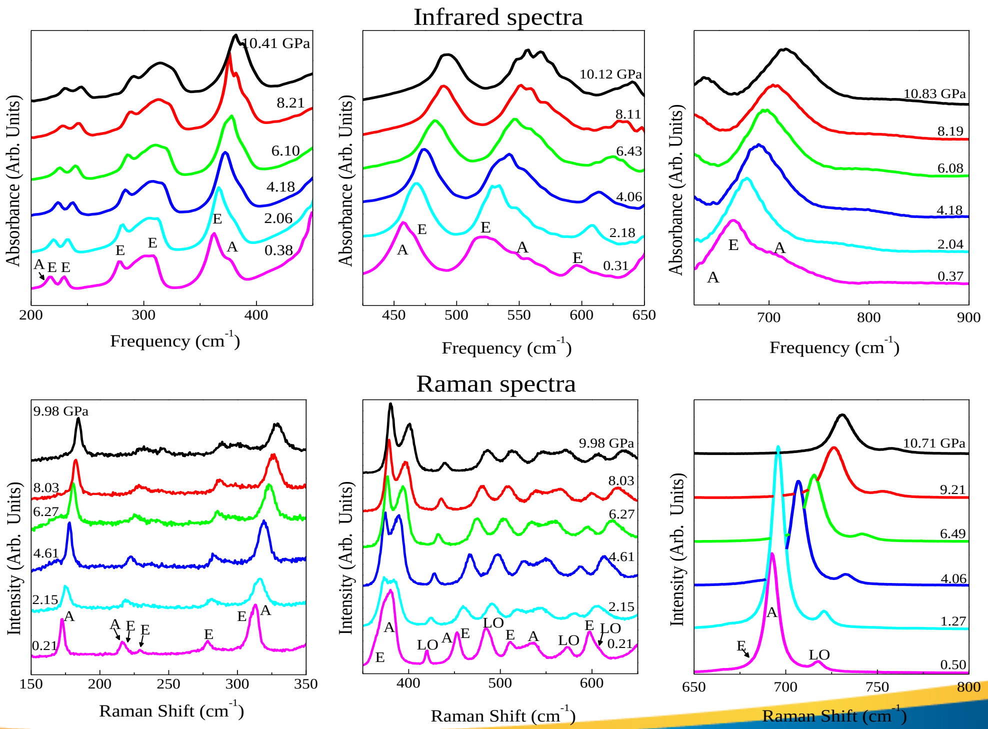
Multiferroic Ni_3TeO_6

- Ferroelectric and antiferromagnetic in ground state
- Temperature-magnetic field phase diagram known
- No previous pressure studies
- Structure is more complex than it at first appears
  - Three unique NiO_6 configurations
  - Empty O_6 cages throughout



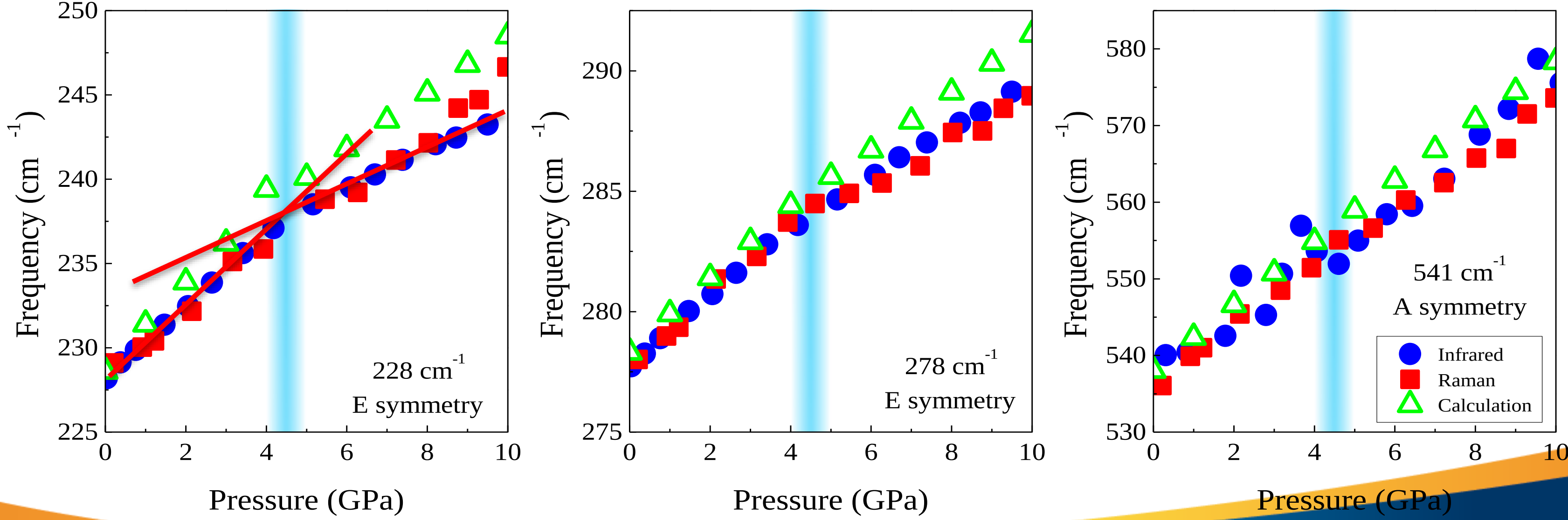
High pressure spectra

- Measured both infrared and Raman
- Can assign all modes based on calculations and previous work



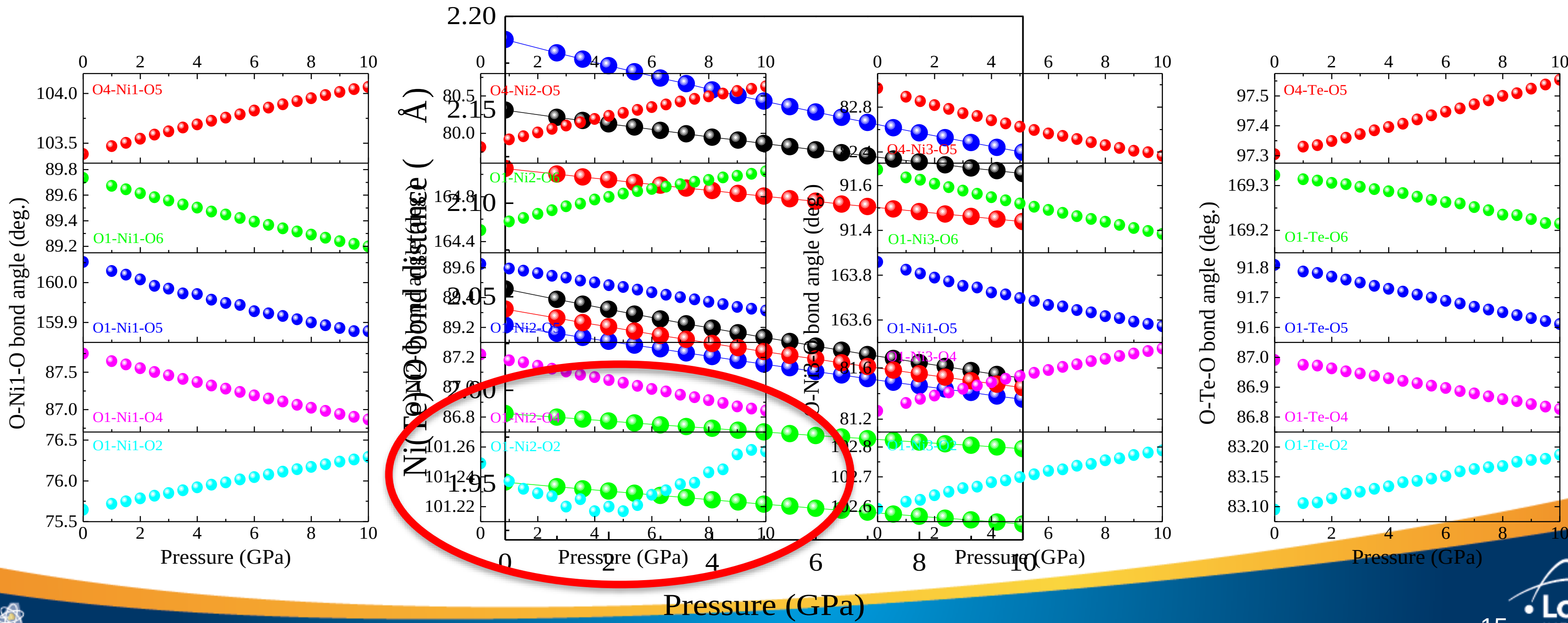
Subtle changes in spectra

- Tracking mode frequencies reveals reduced compressibility above 4 GPa
  - Slopes for several modes decrease here
- Supported by calculations of spectrum using structure under pressure
- Why only some modes?



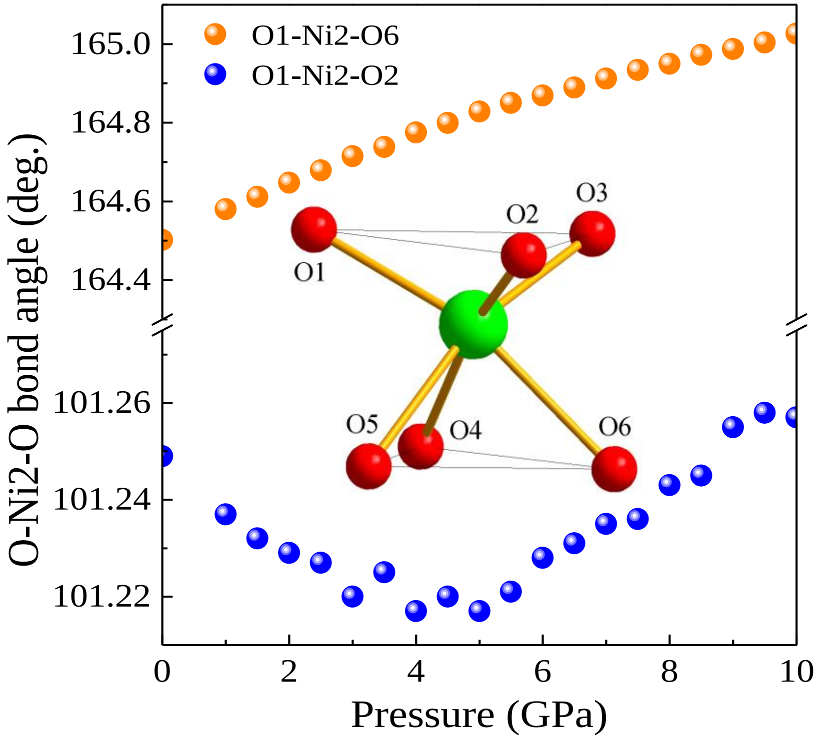
What causes the slope change?

- Use calculated structures to look for clues
- Bond lengths all change linearly – nothing to learn
- Bond angles also change linearly – except for one!



What do we learn?

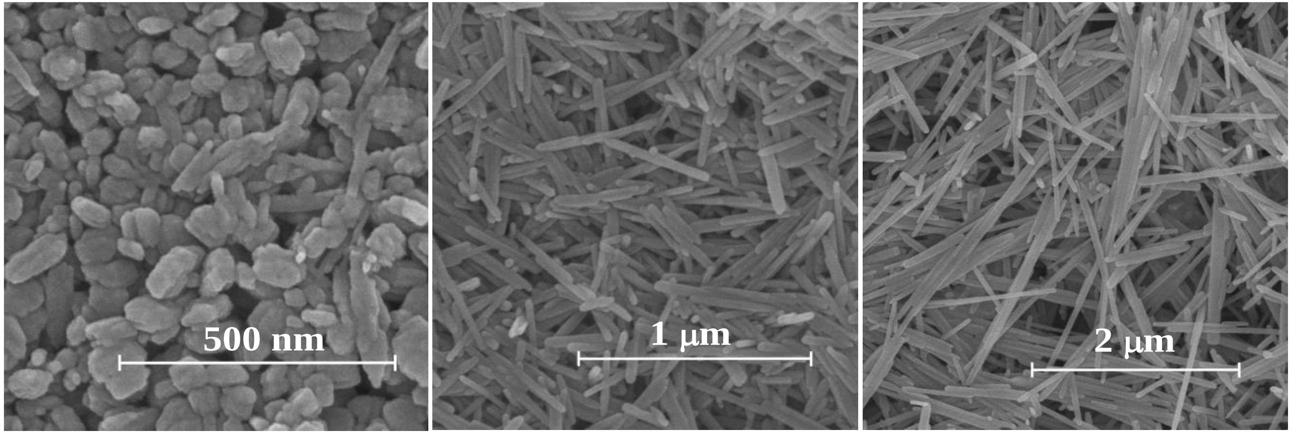
- Used detailed analysis to reveal cause of slope change
- Vibrations of atoms near the empty pocket all displayed the slope change
- Pocket compresses easily up to 4 GPa, then stiffens as atoms get closer
- Changes to magnetic exchange in line with preliminary measurements

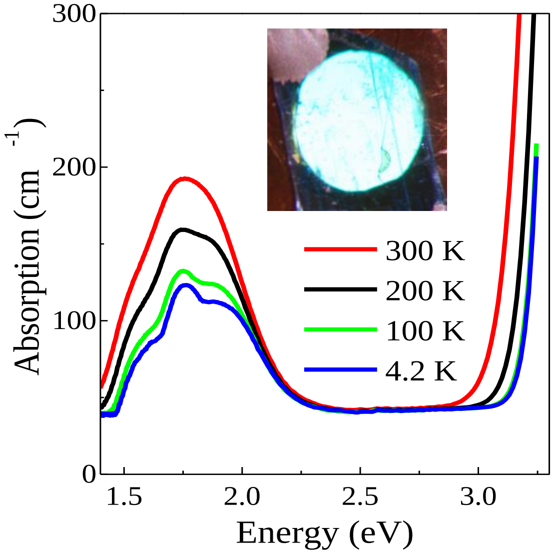


O'Neal, Phys. Rev. B **98**, 184101 (2018)

$CuGeO_3$ nanorods

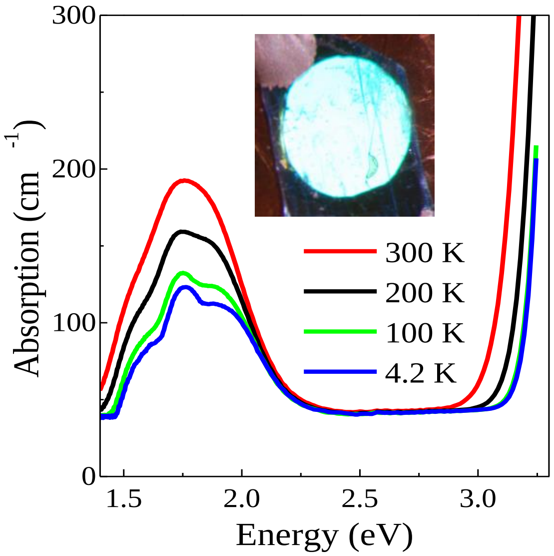
- Spin-Peierls transition at low temperature
- Bulk has been studied for over 20 years
- Can now grow nanorods – new way to tune the properties
  - Control of nanorod length, keeping diameter similar
  - Spin-Peierls transition suppressed in shortest rods

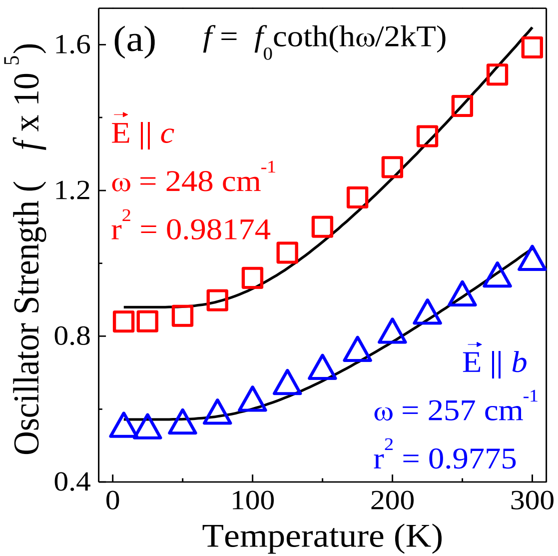




Vibronic coupling

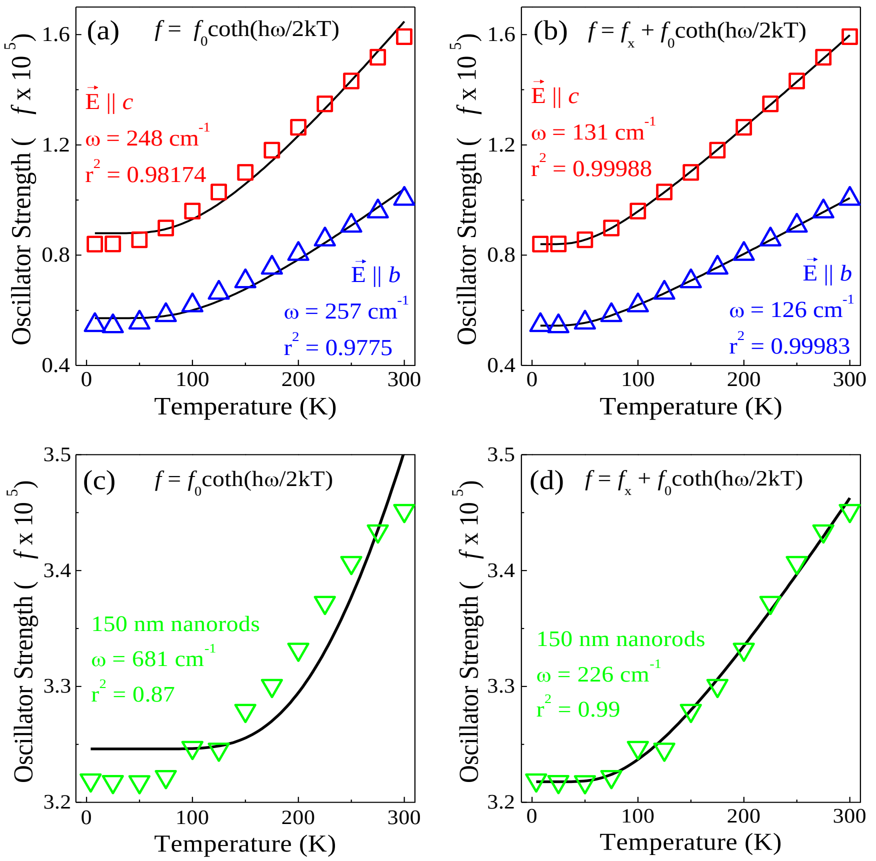
- d-d electronic transition is formally forbidden
  - Activated by odd parity phonon (IR-active)
- Temperature dependent oscillator strength can be modeled
  - Can indicate which phonon(s) are activating the transition





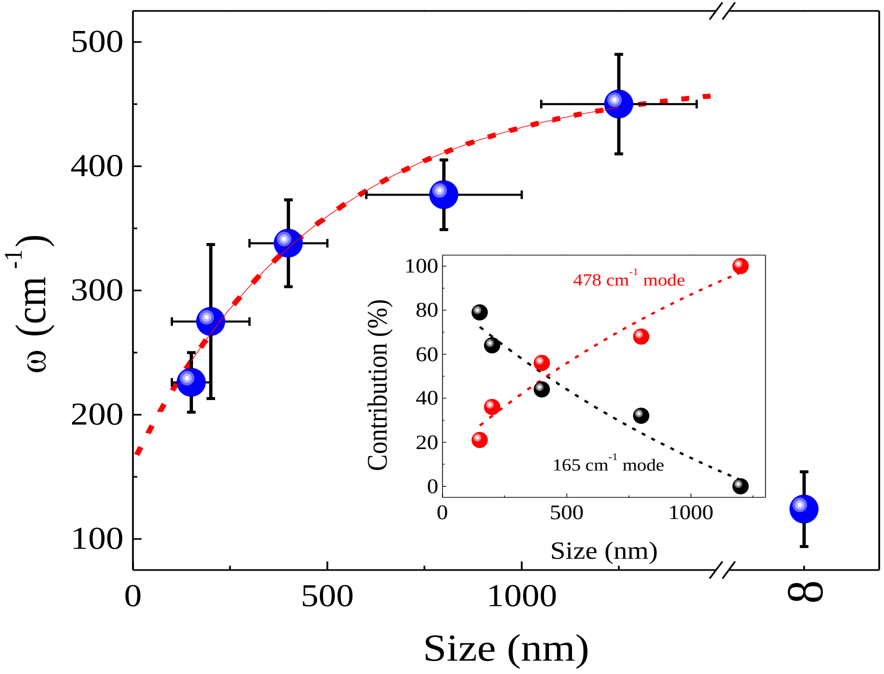
Vibronic coupling model limitations

- Typical vibronic coupling model did not work for nanorods
- Added a temperature-independent constant, f_x
- Slight improvement in fit for bulk
  - Significant difference in phonon frequency
- Needed a physical basis for constant
  - Defects and edge effects
  - Distortions in crystal structure



What do we learn?

- New model worked for all nanorods
- Could track size dependence of coupled phonon frequency
- Crossover in most important phonon below rod length of 500 nm
  - Blue color comes from different origin
- New model can now apply to all nanomaterials



O'Neal, Phys. Rev. B 96, 075437 (2017)

Outline

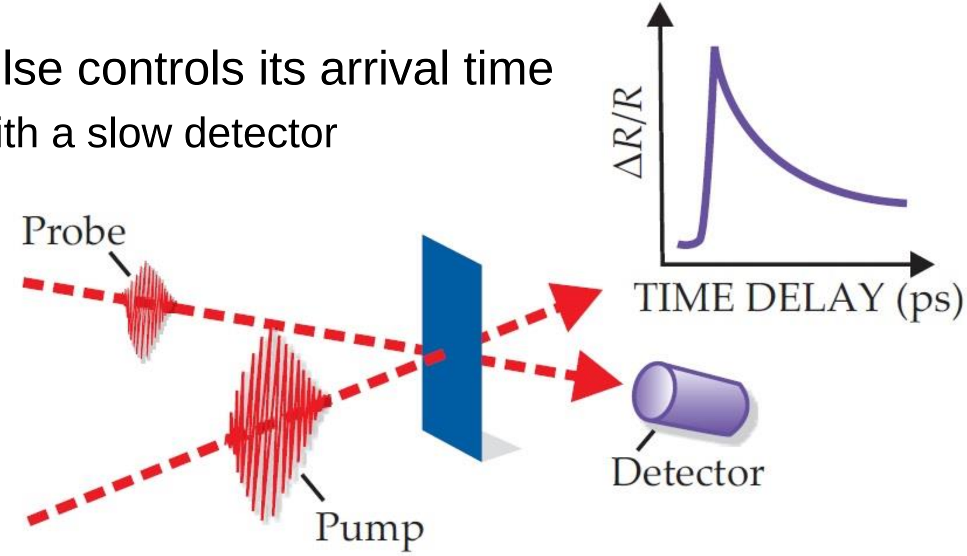
- FTIR and Raman
  - Pressure-induced dimensionality crossover in Cu-3Cl(pyd)
  - Local structure changes in Ni_3TeO_6 under pressure
  - Size-dependent vibronic coupling in $CuGeO_3$ nanorods

- **Ultrafast spectroscopy**
  - Carrier dynamics of $EuCd_2As_2$

- Summary and Acknowledgements

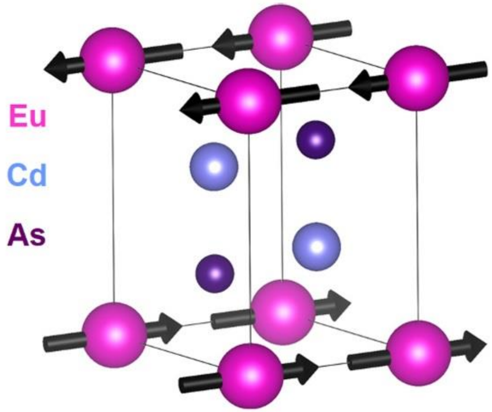
Ultrafast spectroscopy

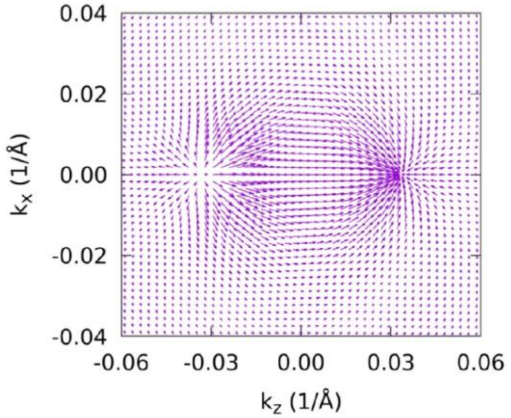
- Laser pulse excites material
- Second, weaker pulse measures changes
- Varying the path length of the second pulse controls its arrival time
  - Allows for ultrafast measurements even with a slow detector
- Spectral selectivity, high sensitivity, small focal size, femtosecond timescale



$EuCd_2As_2$ – magnetic Weyl semimetal(?)

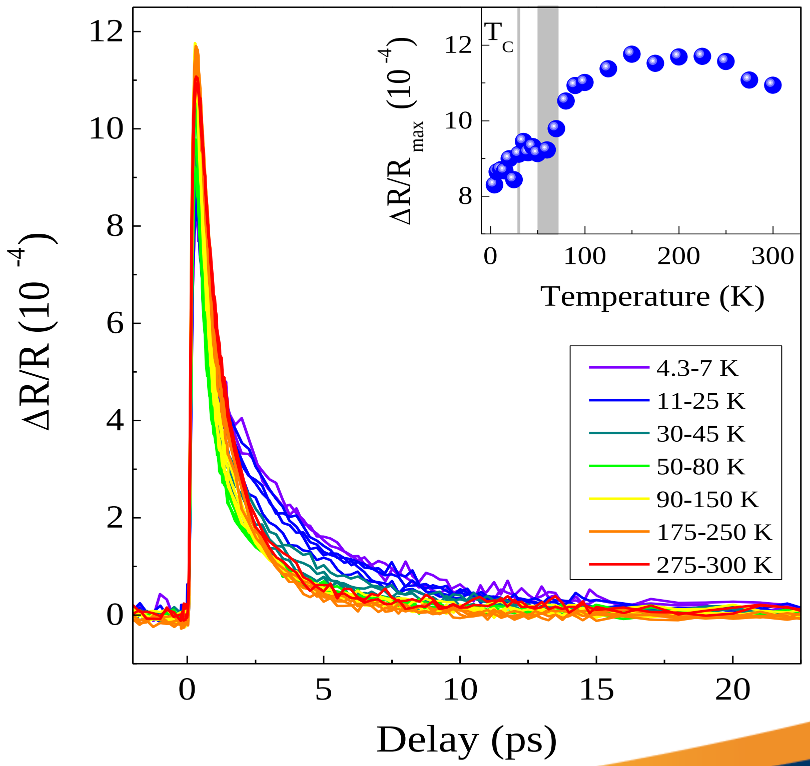
- Magnetic derivative of Cd_2As_3
- Growth conditions affect magnetism
  - (FM) T_c = 30 K or (AFM) T_N = 9 K
- Spins forced to align out of plane leads to Weyl semimetal with one pair of nodes
- Other measurements have been inconclusive





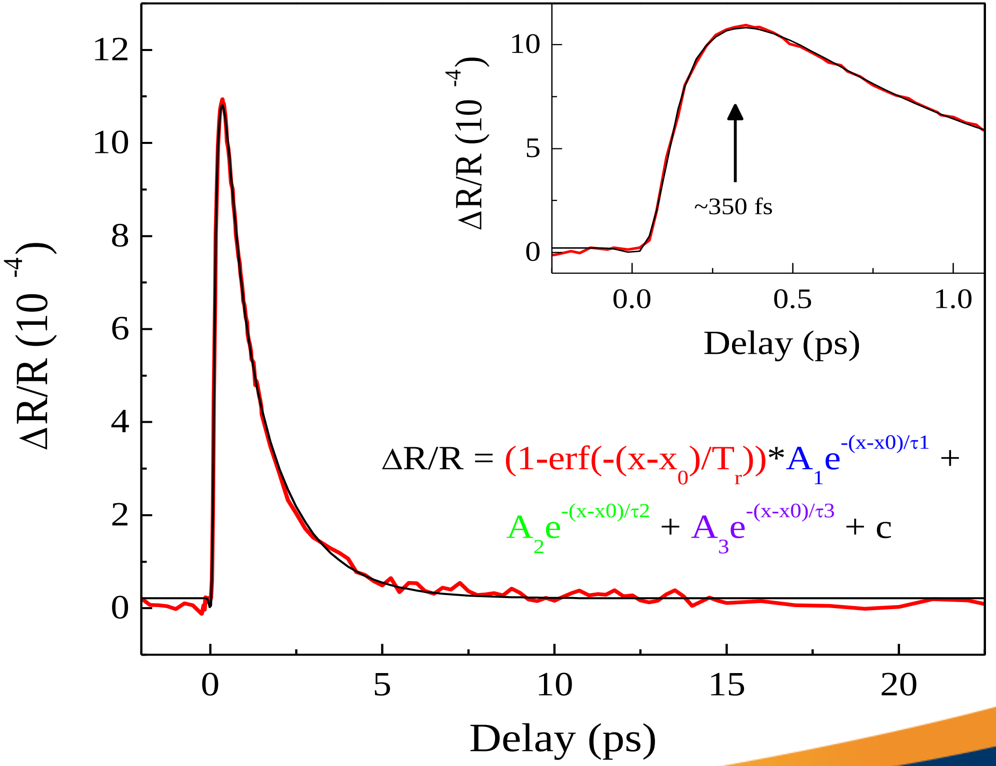
Across the magnetic ordering transition

- Measure as function of temperature
  - Observe changes across T_C = 30 K
- Overall changes appear gradual
  - Magnitude rises then falls
  - Timescale follows similar trend
- Need to fit data to learn more



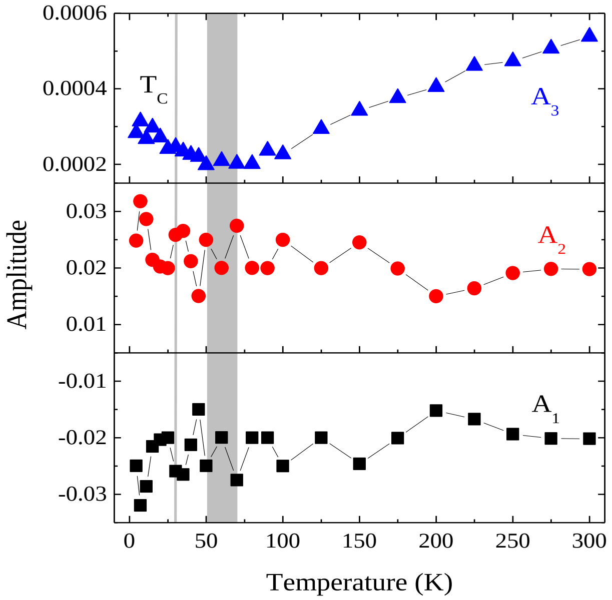
Fitting the data

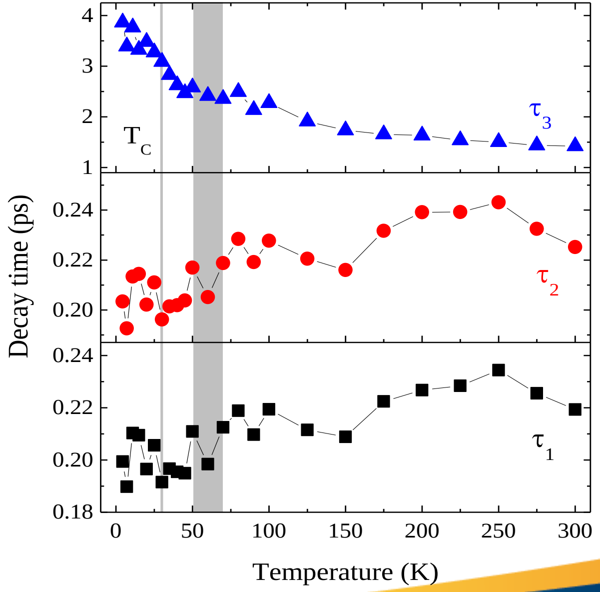
- Fit data at each temperature to extract parameters
- Model is complex
  - Rise from laser pulsewidth
  - Slow rise process
  - Two decay processes
    - Electron-phonon relaxation
    - Spin-phonon relaxation
- Follow parameters as function of temperature to look for changes across T_C



How does magnetism affect dynamics?

- Subtle signs of spin-charge coupling across T_C
- Much stronger changes near 70 K
  - Attributed to short-range, in-plane magnetic fluctuations

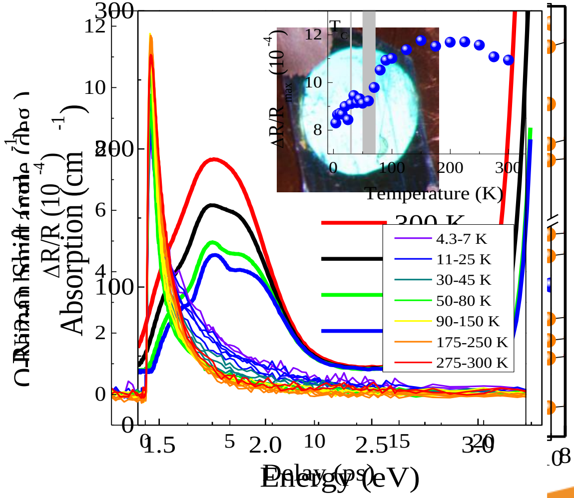




Summary

- Spectroscopy is powerful and non-destructive technique that can be used to study a wide range of materials
  - Can probe phase transitions with temperature, magnetic field, and pressure

- Detailed data analysis is key to deep understanding
  - Hydrogen bond formation in $CuF_2(H_2O)_2$(3-chloropyridine)
  - Local structure changes in Ni_3TeO_6
  - Size-dependent vibronic coupling in $CuGeO_3$ nanorods
  - Ultrafast carrier dynamics in $EuCd_2As_2$



Acknowledgements

- $CuF_2(H_2O)_2$(3-chloropyridine)
  - Jan Musfeldt (advisor)
  - Puru Jena (calculations)
  - Zhenxian Liu (high pressure)
  - John Schlueter (synthesis)
- $CuGeO_3$
  - Jan Musfeldt (advisor)
  - Xue-Tai Chen (synthesis)
- $EuCd_2As_2$
  - Dmitry Yarotski (advisor)
  - Rohit Prasankumar (advisor)
  - Paul Canfield (synthesis)
- Funding
  - National Science Foundation
  - Department of Energy
  - CATS